AN INVESTIGATION OF THE INFLUENCE OF
TEMPERATURE ON THE ADSORPTION OF IODIDE ON COPPER

JOSEPH H. PIRKL

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AN INVESTIGATION OF THE INFLUENCE

OF

TEMPERATURE ON THE ADSORPTION OF IODIDE ON COPPER

by

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Submitted in partial fulfillment
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PREFACE

This investigation of the influence of temperature on the adsorption of iodide on copper was conducted at the United States Naval Postgraduate School during the last half of the academic year 1953-54.

The investigation was largely exploratory, designed to uncover any large effects over a convenient temperature interval, and involved a relatively new approach which necessitated the development of new experimental techniques and procedures. The experimental data, techniques, and procedures presented in this paper will serve as a basis and aid for future continuance of this investigation at this institution.

The writer would like to express his appreciation to Professors W.W. Hawes and G. F. Kinney of the United States Postgraduate School Staff for their suggestions and guidance.

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CHAPTER I

INTRODUCTION

1. General

The property known as adsorption was described first by the Swedish chemist Scheele who observed that gases were taken up by charcoal. He showed that a piece of charcoal, heated to drive out air and then allowed to rise through a column of mercury which was enclosing some air in a tube, took up air so strongly that the level of the mercury rose substantially in the tube.* The fact that charcoal removes organic colors from solutions also has been known a long time. Although this property of adsorption is fundamentally involved in many chemical processes, its importance has only been fully realized in the recent years.

Adsorption is a property of surfaces. A surface exists whenever two phases such as solid and liquid, solid and gas, liquid and liquid, or liquid and gas are in contact. The "interface" is the layer of matter which forms a surface to each of the two phases. Adsorption results in either an increase or decrease of some constituent of this interfacial layer.

The two main types of adsorption are Chemisorption-in which the adsorbed substance is held to the adsorbent by chemical bonds and Physical-which is a physical bonding of adsorptive to the surface of the adsorbent by van der Waal's forces. The two types of adsorption just mentioned can be dealt with from energy considerations also, using the magnitude of adsorption energy as a classification basis. In relation to adsorption at

*Gucker & Meldrum (6), p. 510

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solid surfaces, processes which involve large energy changes are called "chemisorptions".

There is also the term "Activated Adsorption" which is applied to adsorptions on solid surfaces which proceed slowly and at reasonable temperatures. In this case, it has been theorized that this reaction has a certain energy threshold and only those molecules possessing sufficient energy will be adsorbed. The rate of reaction for this process is increased by a rise in temperature.

Let us examine the general process of adsorption at a solution-solid interface. Here we have the invariable feature of competition between solvent and solute molecules for the surface. Upon the introduction of a solid adsorbent into the solution, there is an immediate struggle between solvent and solute molecules for the surface.*

Studies with adsorbents and mixtures have shown that at the ends of the concentration ranges, the component present in smaller amount was most always preferentially adsorbed.** In general, adsorption from solution is like adsorption of gases; it is however selective. Either the solvent or solute is adsorbed, but not both, and if several solutes are present one will usually be more adsorbed than another.

Unless different sites are involved, it would be expected that the adsorption of one molecule would eliminate the adsorption of another since the surface area is limited. One molecule of adsorptive may prevent adsorption of several other molecules of solvent (for example) if the adsorbed molecule situates itself in such a way on the surface "checkerboard"

* Cassidy, (4), p. 35
** Bartell & Sloan; Jones & Outridge; Patrick & Jones; Williams: (1), (8), (10), (12)

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so as to block access to neighboring sites. A further influence on adsorption would be the lateral attraction between neighboring adsorbed molecules which may aid the accumulation of adsorptive on the surface.

The nature of the surface of the solid adsorbent plays a tremendous role in adsorption. In this connection the following direct quotation from Cassidy (4) will be pertinent:

> On a plane, crystalline, chemically homogeneous surface the disposal of sites at which adsorption can occur will, as Langmuir has pointed out, be in a regular pattern. In an amorphous surface a certain regularity may or may not be still present...The spaces available on a plane crystal surface may be of several kinds, but the regularity of the surface may lead to some sort of stoichiometric relation in the adsorption of different substances.......At edges and corners of the adsorbent certain molecules will be in a somewhat exposed condition--perhaps in a strongly curved region of the surface--which may leave them with more capability for interaction than their less exposed neighbors. Such molecules might be more active in adsorbing than others, since the lowering of free energy that would occur in the process would be greater for them than for their neighbors......If the surface were rough, then more of the surface molecules would be in an exposed condition, such as that described above, and the roughness might be conducive to an increase in adsorption of small molecules per unit number of surface molecules over the plane surface. With large molecules, the effect might be of the opposite kind.......If the surface contains capillaries and fissures, then the adsorption may be favored for small molecules than can enter the capillaries ....larger molecules might not be able to enter the capillaries and have, because of their size, considerable adsorption surface excluded to them.......If the surface is not homogeneous, then the resultant effects can be very complicated indeed....The area occupied by the molecules in the interface will play a role in the adsorption because a molecule that covers many active spots,for example, a chain molecule, will be more adsorbable than a monomer. This is because of the tendency of molecules to remain in the adsorbed state diminishes with increasing chain length. Here, also, not only size, but shape plays a role.....A large molecule may displace several small ones; or a large molecule may block off, without occupying, several sites where adsorption might otherwise occur. The adsorption of small molecules may not be appreciably affected by the presence of large ones if the small can reach areas of the surface inaccessible to the large.....The mutual interactions between adsorbed molecules which may cause them to adhere laterally may influence the quantity adsorbed by allowing

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the adsorbed film to bridge roughness and fissures in the adsorbent.

Smooth surfaces for adsorption studies are very difficult to obtain. Frazer, Patrick, and Smith (5) noted that the properties of a glass surface are much different after the glass was cleaned in an acid bath. Brown and Uhlig (3) made surface studies of chrome plated nickel strips before and after an etching with hydrochloric acid. Photomicrographs showed numerous cracks and fissures. Another reference to the acid treatment of surface area and its effects is given by Heymann and Boye (7) who carried out adsorption experiments with fatty acids from water solution on gold and noted that the amount of adsorption was decreased when the gold was first treated with hot nitric acid.

Measurements of adsorption from a solution onto a solid surface has usually been based on the measurement of the concentration of the solution before the adsorbent is introduced and after equilibrium is established. It must be assumed that the solvent is not adsorbed to any appreciable extent and that the components of the liquid phase do not dissolve in the adsorbent. Thus when working with quite dilute solutions, the adsorption of the solvent is usually neglected, as the solute is preferentially adsorbed.

The field of adsorption is extremely vast and complicated and there are many related phenomena whose examination constitute a considerable problem; such as reversibility of the process, typing of bonding, accompanying energy changes, area occupied by the adsorbed molecules, surface effects, and the influence of conentration and temperature.

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2. Experimental

The basic research problem was to conduct an investigation of the effect of temperature on adsorption from solution to a solid surface. Very little has been reported in the literature on the influence of temperature on adsorption of a solute from liquid phase, though numerous studies have been made on gas adsorption. This is due, at least in part, to the limited temperature range available in a liquid and the insensitivity of measurements of concentration changes on which amounts adsorbed have been based. By use of a radioactive adsorptive, it is possible to directly measure quantities adsorbed and thus markedly increase the ability to detect small changes in adsorption. Study of temperature effects then becomes practical with restricted temperature ranges.

Bernard, Davoine, and Hertz (2) report the use of tritolyl phosphate solution containing P^{32} in adsorption studies with glass disks. Initial layers formed at room temperature rapidly reached 12 Angstroms and increased in thickness slowly over a period of weeks. Layers initially formed and saturated at 220° C rapidly made an equilibrium layer of about 50 Angstroms.

King and Schochet (9) have studied the adsorption of silver salts on silver, using Ag^{110} tracer. When the silver surface was untreated, it adsorbed less than a monolayer; yet when the metal was cleaned with dilute nitric acid, large amounts of Ag^{110} were adsorbed.

Rydberg and Rydberg (11) performed work on adsorption on glass and polyethylene from solutions of thorium and thorium complexes. Adsorption was measured with a G-M liquid counter as the difference between reference and test sample.

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The system copper—iodide ion was chosen for investigation. Copper in the form of thin disks served as the adsorbent. Iodide ion was present in an aqueous sodium iodide solution. I^{131} was chosen because it was readily available, had a sufficiently long half life (8 days) to adequately span the period of observations at a single temperature and yet not long enough to cause a serious contamination hazard, and possessed a convenient energy of disintegration (0.6 Mev, Beta emitter).

The results of the present investigation indicate that a rise in temperature is accompanied by an increase in the adsorption of iodide ion on a copper surface. The adsorbed activity at any total immersion time and at a given temperature and concentration can be represented by a function of the form:

$$\alpha = k \left(A e^{-a/t} + B e^{-b/t} \right)$$

where "A", "B", and "a" are constants independent of temperature, "k", "b" are constants for a given temperature and concentration, and "t" is the total time of immersion.

For the present data the function becomes:

$$\alpha = k \left(19.1\, e^{-0.102/t} + 146\, e^{-b/t} \right)$$

where "α" is measured adsorbed activity expressed as d/min x 10^{-3} and "t" is in hours.

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1. General procedure

Acid cleansed copper disks are suspended in a glass beaker containing
an aqueous solution of I^{131} at a known concentration and temperature. A
temperature bath serves as a means of temperature control. After an arbi-
trarily chosen immersion time, the disks are removed from the solution,
dried with tissue, and their activity measured. The process is repeated
over successive time intervals, so that each measured activity is intra-
polated back to "zero" time—time at which that particular temperature
run was begun.

The copper disks are roughly the size and shape of a quarter. To
facilitate their suspension in solution a small hole is drilled near the
edge of each disk in order to permit the attachment of a thin copper wire.
The other end of the wire is hooked over the rim of the glass beaker and
serves to suspend the disk in the radioactive solution. In order to assure
the uniformity of surface the disks are treated to a three minute im-
mersion in 6 N HNO_3, followed by 4 washings with distilled water before
they are marked for use. It was further determined that the thickness of
each disk was sufficient to shield out the radiation from the adsorbed
activity on the reverse side.

The radioactive solution is prepared using I^{131} as furnished by the
AEC in 3 cc. vials containing approximately 100 micro-curies per vial as
of make-up date. Since temperature was to be the only variable desired,
the concentrations of the solutions made up for each separate temperature

run were maintained as nearly constant as possible and furthermore a level of concentration was chosen (approximately 0.280 u.c./ml) which would give a reasonable initial counting rate on the G-M counter. A total solution volume of 250 ml. was found to be most convenient to work with. The specific activity of the solution was determined prior to, and at the end of each temperature run. This was done as a check to see if any abnormal losses of activity had occurred.

The measuring equipment consisted of a CP-370 D Radiac Computer Indicator with a TGC-1 G-M tube of the thin mica (2.3 mg/cm^2) end window type, which was provided with a shielded holder giving a choice of counting positions. The G-M tube was carefully calibrated before any experimentation was begun. Calibration data is attached as Part 2 of the Appendix. Use of this calibration data permits the expression and tabulation of all measurements of adsorbed activities in terms of d/min.

2. Tabulation of Data:

RUN # 1

Temperature 23°C, "Zero time"—0930, 3/8/54, Solution volume—250 ml.

Determination of initial solution concentration:

Sample	Vol. (ml)	Counts	Sec.	Corr. Cps	Conc. in u.c./ml	Avg.
1	0.106	8192	57.5	142.5	0.286	0.284
2	0.103	8192	58.0	141.2	0.282	

Data on 3/8/54: (Avg. bkgrd. 30 cpm.)

Time	Sample	$1/t$ (hr^{-1})	Counts	Sec.	Cpm corr. for bkgrd. & dead time	Avg.	d/min as of 0930 3/8/54
0930	1	12	8192	865.5	540		
"	2	"	4096	381	616		
"	3	"	"	472.7	492	512	5,660
"	4	"	"	562	408		
1000	5	"	"	427.5	546		
"	6	"	"	491.2	472		
1230	1	7.5	4096	281.5	847		
"	2	"	"	259	921		
1245	3	"	"	367.6	640	767	8,480
"	4	"	"	369.5	637		
1300	5	"	"	288.4	837		
"	6	"	"	328	721		

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1310	1	5	4096	235.5	1015		
"	2	"	"	218	1102		
1320	3	"	"	255	932	1012	11,200
"	4	"	"	319	740		
1335	5	"	"	183.5	1317		
"	6	"	"	253.6	942		
1345	1	3	4096	186	1296		
"	2	"	"	166	1458		
1355	3	"	"	201.8	1195	1323	14,650
"	4	"	"	227	1055		
1410	5	"	"	156.5	1549		
"	6	"	"	174	1389		
1435	1	2	8192	301	1612		
"	2	"	"	265	1840		
1445	3	"	"	314.2	1542	1745	19,300
"	4	"	"	339.5	1427		
1455	5	"	"	230	2126		
"	6	"	"	254	1921		
1510	1	1	8192	130.2	3800		
"	2	"	"	159.4	3085		
1520	3	"	"	155.8	3165	3686	40,750
"	4	"	"	133.8	3690		
1530	5	"	"	129.5	3815		
"	6	"	"	108.5	4565		

Following data on 3/10/54, 0930: (Avg. bkgrd. 38 cpm.)

Time	Sample	1/t (hr^{-1})	Counts	Sec.	Cpm. corr. for bkgrd. & dead time	Avg.	d/min as of 0930 3/8/54
0930	1	0.5	12,288	101	7460		
"	2	"	"	107.5	7000		
"	3	"	"	131	5690	6407	84,500
"	4	"	"	161.8	4580		
"	5	"	"	109	6880		
"	6	"	"	110	6830		

Following data on 3/12/54: (Avg. bkgrd. 42 cpm.)

Time	Sample	1/t (hr^{-1})	Counts	Sec.	Cpm. corr. for bkgrd. & dead time	Avg.	d/min as of 0930 3/8/54
1430	1	0.125	12,288	55.2	13,960		
"	2	"	"	57.1	13,380		
"	3	"	"	65	11,750	12,380	189,000
"	4	"	"	80	9,460		
"	5	"	"	60	12,800		
"	6	"	"	59.5	12,930		

Following data on 3/15/54: (Avg. bkgrd. 38 cpm.)

Time	Sample	1/t (hr^{-1})	Counts	Sec.	Cpm. corr. for bkgrd. & dead time	Avg.	d/min as of 0930 3/8/54
1000	1	0.0133	16,384	37	29,380		
"	2	"	"	41	26,300		
"	3	"	"	41.5	25,800	24,455	496,000
"	4	"	"	67.5	15,350		
"	5	"	"	44	24,300		
"	6	"	"	42	25,600		

RUN # 1 (Cont.)

Determination of final solution concentration: (0900, 3/15/54)

Sample	Vol. (ml)	Counts	Sec.	Corr. Cps	Conc. in u.c./ml	Avg.
1	0.100	8192	106	77.3	0.155	0.154
2	0.102	8192	110	74.5	0.153	

Temperature 65°C, "Zero-time"--1000, 3/26/54, Solution volume--250 ml.

Determination of initial solution concentration:

Sample	Vol. (ml)	Counts	Sec.	Corr. Cps	Conc. in u.c./ml.	Avg.
1	0.110	8192	85.6	96.6	0.262	0.260
2	0.102	8192	94	88.4	0.258	

Data on 3/26/54: (Avg. bkgrd. 42 cpm)

Time	Sample	1/t (hr⁻¹)	Counts	Sec.	Cpm corr. for bkgrd. & dead time	Avg.	d/min as of 1000 3/26/54
1000	1	12	4096	417	550		
"	2	"	1024	81.8	712		
"	3	"	"	93	622	617	6,820
"	4	"	"	84.8	687		
"	5	"	"	113	506		
"	6	"	"	92.8	624		
1045	1	7.5	2048	101.5	1176		
"	2	"	"	108	1102		
"	3	"	"	126.5	936	980	10,830
"	4	"	"	103	1158		
"	5	"	"	185	627		
"	6	"	"	152	772		

1145	1	5	2048	93.8	1277		
"	2	"	"	102	1178		
"	3	"	"	89	1347	1298	14,370
"	4	"	"	75	1610		
"	5	"	"	102	1178		
"	6	"	"	99.8	1198		

Following data on 3/27/54: (avg. bkgrd 42 cpm)

1000	1	3	2048	70.6	1710		
"	2	"	"	71.8	1678		
"	3	"	"	64	1890	1806	21,800
"	4	"	"	65.8	1839		
"	5	"	"	69.2	1748		
"	6	"	"	61.5	1972		
1100	1	2	4096	81.4	3008		
"	2	"	"	85.2	2860		
"	3	"	"	78.2	3128	3023	36,400
"	4	"	"	76.6	3210		
"	5	"	"	89	2740		
"	6	"	"	77.0	3190		
1200	1	1	8192	88.8	5600		
"	2	"	"	88.4	5630		
"	3	"	"	76.4	6540	5780	70,000
"	4	"	"	85	5860		
"	5	"	"	104	4770		
"	6	"	"	79.5	6220		

RUN # 2 (Cont.)

Following data on 3/29/54: (Avg. bkgrd. 40 cpm)

0955	1	0.5	12,288	96	7850		
"	2	"	"	107.8	6970		
"	3	"	"	82.6	9150	7675	110,000
"	4	"	"	102.4	7330		
"	5	"	"	123.6	6050		
"	6	"	"	87	8700		
1500	1	.167	16,384	74.6	13,820		
"	2	"	"	93.8	10,900		
"	3	"	"	96.8	10,500	12,000	175,000
"	4	"	"	87.6	11,650		
"	5	"	"	100	10,150		
"	6	"	"	69	14,970		

Determination of final solution concentration: (0900, 3/30/54)

Sample	Vol. (ml)	Counts	Sec.	Corr. Cps	Conc. in u.c./ml.
1	0.100	8192	130	63.2	0.188

Applying decay factor gives a value of <u>0.204 u.c./ml as of 1500, 3/29/54</u>

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Temperature 45°C, "Zero time"—1500, 3/30/54, Solution volume—250 ml.

Determination of initial solution concentration:

Sample	Vol. (ml)	Counts	Sec.	Corr. Cps	Conc. in u.c./ml
1	0.105	8192	86	96.6	0.275

Data on 3/30/54: (Avg. bkgrd, 40 cpm)

Time	Sample	$1/t$ (hr^{-1})	Counts	Sec.	Cpm corr. for bkgrd. & dead time	Avg.	d/min as of 1500 3/30/54
1500	1	12	4096	72.6	3380		
"	2	"	"	69.4	3540		
"	3	"	"	93.8	2610	2,750	30,400
"	4	"	"	95.8	2558		
"	5	"	"	115	2118		
"	6	"	"	106.2	2290		
1545	1	7.5	8192	89.5	5570		
"	2	"	"	82.6	6675		
"	3	"	"	123	4010	4,177	46,200
"	4	"	"	154.2	3180		
"	5	"	"	176.5	2770		
"	6	"	"	171.4	2855		
1630	1	5	8192	64	7850		
"	2	"	"	57	8850		
"	3	"	"	93	5340	5,655	62,500
"	4	"	"	117	4220		
"	5	"	"	130	3790		
"	6	"	"	127	3880		

Following data on 4/1/54:   (Avg. bkgrd. 37 cpm)

1000	1	3	16,384	135.4	7415		
"	2	"	"	135.4	7415		
"	3	"	"	197	5030	5,780	74,700
"	4	"	"	178	5600		
"	5	"	12,288	157.2	4730		
"	6	"	"	166	4480		
1015	1	2	12,288	87	8700		
"	2	"	"	87.6	8630		
"	3	"	"	125	5985	6,784	87,400
"	4	"	"	117.2	6450		
"	5	"	"	129	5800		
"	6	"	"	135	5540		
1100	1	1	12,288	68	11,250		
"	2	"	"	73	10,450		
"	3	"	"	95	7,860	8,646	112,000
"	4	"	"	99.4	7,580		
"	5	"	"	103	7,310		
"	6	"	"	101.6	7,415		
1200	1	0.5	12,288	61.8	12,400		
"	2	"	"	62	12,390		
"	3	"	"	73.8	10,340	10,473	136,000
"	4	"	"	85	8,920		
"	5	"	"	81.6	9,280		
"	6	"	"	79.8	9,510		

Bkgrd was 60 cpm for the following:

1630	1	0.167	16,384	52.8	19,800		
"	2	"	"	59.8	17,400		
"	3	"	"	67.2	15,350	15,723	208,000
"	4	"	"	78.8	13,070		
"	5	"	"	74.6	13,800		
"	6	"	"	69	14,920		

Determination of final solution concentration: (1630, 4/1/54)

Sample	Vol. (ml)	Counts	Sec.	Corr. Cps	Concentration in u.c./ml
1	0.100	8192	111.4	73.8	0.220

Temperature 35°C, "Zero-time"--1400, 4/5/54, Solution volume--250 ml.

Determination of initial solution concentration:

Sample	Vol. (ml)	Counts	Sec.	Corr. Cps	Concentration in u.c./ml	Avg.
1	0.100	8192	93.2	88.9	0.266	0.269
2	0.104	8192	88	94.4	0.272	

Data on 4/5/54: (Avg. bkgrd, 40 cpm)

Time	Sample	$1/t$ (hr^{-1})	Counts	Sec.	Cpm corr. for bkgrd. & dead time	Avg.	d/min as of 1400 4/5/54
1400	1	12	1024	103	557		
"	2	"	"	85.8	672		
"	3	"	"	149	373	542	6000
"	4	"	"	101.2	568		
"	5	"	"	106	541		
1430	1	7.5	2048	120	988		
"	2	"	"	124.2	953		
"	3	"	"	172	677	853	9,430
"	4	"	"	122.2	968		
"	5	"	"	170.8	682		
1455	1	5	2048	98.8	1210		
"	2	"	"	91.8	1307		
"	3	"	"	114.8	1035	1100	12,150
"	4	"	"	113.5	1045		
"	5	"	"	131	901		

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1540	1	3	2048	70.8	1710		
"	2	"	"	65.4	1851		
"	3	"	"	76	1587	1625	17,950
"	4	"	"	79.6	1514		
"	5	"	"	82.2	1462		
1600	1	2	4096	114.8	2118		
"	2	"	"	85.6	2858		
"	3	"	"	112	2169	2,246	24,800
"	4	"	"	121.5	1994		
"	5	"	"	116	2095		

Following data on 4/6/54: (Avg. bkgrd., 45 cpm)

1000	1	1	8192	109	4520		
"	2	"	"	94.5	5250		
"	3	"	"	113.8	4330	4,542	53,950
"	4	"	"	104	4772		
"	5	"	"	128.2	3840		
1110	1	0.5	8192	61.5	8200		
"	2	"	"	52.2	9670		
"	3	"	"	68.6	7300	8,014	95,400
"	4	"	"	59.4	8450		
"	5	"	"	77.4	6450		

Following data on 4/7/54: (Ave. bkgrd. 45 cpm)

1000	1	0.167	20,480	95.8	13,440		
"	2	"	"	69.8	18,700		
"	3	"	"	92.2	13,970	15,846	206,000
"	4	"	"	68.6	19,100		
"	5	"	"	91.6	14,020		

Determination of final solution concentration: (4/7/54)

Sample	Vol. (ml)	Counts	Sec.	Corr. Cps	Conc. in u.c./ml	Avg.
1	0.100	8192	114.2	71	0.216	
2	0.100	8192	115.6	70.3	0.212	0.214

3. Summary and discussion of results

The previously tabled experimental data is presented graphically as Figures 1-5. Here the adsorbed activities at the different temperatures are plotted against reciprocal time. The composite graph (Fig. 1) reveals that the initially adsorbed activities follow the same regular increase for some time (i.e.—early portions of all curves have the same slope), and then deviate substantially in rate of increase as one approaches the value of $1/t = 0$. As the temperature increases this deviation also increases. The initial straight line portion of any one of the curves can be expressed by a function of the form $Ae^{-a/t}$, where "A" is the intercept with the line $1/t = 0$, "a" is the slope, and "t" is the total immersion time in hours. A similar function $Be^{-b/t}$, where "b" is a constant characteristic for a particular temperature, will give another straight line which when summed graphically with the first will give substantial agreement with the experimental curve over a sufficient range of time (to $1/t = 0.5$). For this latter function, "B" is the intercept and "b" is the slope.

In order to provide for the difference in initially adsorbed activity at the different temperatures, a constant multiplier "k" is introduced; this is a characteristic constant of a given temperature. The general expression for adsorbed activity at any particular temperature and total immersion time is given by the following:

$$\alpha = k \left(Ae^{-a/t} + Be^{-b/t} \right)$$

where "α" is given as d/min x 10^{-3}.

Choosing $23^{\circ}C$ as the reference temperature, and arbitrarily setting

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k = 1, the values of "A" (19.1), "a" (−0.102), "B" (146), and "b" (−1.835) are readily determined. It follows that at a different temperature "kA" and "kB" will be the values of the new intercepts and "b" will be the new slope of the second straight line. The value of "a" we have already mentioned to be independent of the temperature change and will remain constant in value.

From the short table below it will be noted that the value of "k" shows a systematic increase with temperature, while the value of "b" shows a systematic decrease with increasing temperature.

Temperature	k	b	kA	kB
23°C	1	−1.835	19.1	146
35	1.07	−1.480	20.4	156
45	1.12	−1.410	21.4	164
65	1.23	−1.297	23.5	180

In the foregoing table, values for 45°C are based on an arbitrary correction for an unusual surface effect. This is discussed at more length in the last two pages of this summary.

In addition to the composite graph mentioned earlier, there are also attached as Figs. 2–5 the single plots for each temperature run. Both calculated and experimental points are shown in order to demonstrate the agreement between experimental data and the data as calculated from the expression:

$$\alpha = k \left(19.1\, e^{-0.102/t} + 146\, e^{-1.835/t}\right)$$

It is of no great concern here that the theoretical expression does not give agreeable results beyond $1/t = 0.5$. It was developed specifically to substantially hold up to this point and this range is sufficient to demonstrate the influence of temperature.

The calculated α's and experimental α's are presented in tabular form on the pages immediately following, along with the % deviation.

Basic formula: $\alpha = k (19.1e^{-.102/t} + 146e^{-b/t})$

where A = 19.1 = a constant derived as intercept of initial straight line portion of 23°C run with line 1/t = 0

a = -.102 = slope of the initial straight line portion

k = a temperature dependent coefficient, may also involve surface effects

B = 146 = a constant derived as intercept of the second "fitting" straight line for 23°C with line 1/t = 0

b = a temperature dependent coefficient, value of which is the slope of the second straight line

1/t = accumulated immersion time, hr^{-1}

Temp	k	b	$\frac{1}{t}$	calc α	Exp α	% deviation
23°C	1	1.835	12	5.62	5.66	-0.71
			7.5	8.90	8.48	+4.95
			5	11.46	11.20	+2.32
			3	14.68	14.65	+0.20
			2	19.35	19.30	+0.29
			1 '	40.72	40.75	-0.07
			0.5	76.88	84.50	-9.02
35°C	1.07	1.480	12	5.98	6.00	-0.33
			7.5	9.48	9.43	+0.53
			5	12.31	12.15	+1.32
			3	16.05	17.95	-0.56
			2	24.75	24.80	-0.20
			1	54.12	53.95	+0.31
			0.5	94.08	95.40	-1.38

Temp	k1	b	$\frac{1}{t}$	calc α	calc α x k_2	exp α	% deviation
45°C	1.12	1.410	12	6.29	29.40	30.40	-3.30
k = k_1 k_2			7.5	9.97	46.56	47.50	-1.98
where k_2 = 4.67			5	13.02	60.80	61.00	- .33
is a theorized			3	18.20	84.80	74.70	+13.40
surface effect factor			2	27.31	127.5	87.4	
			1	59.52	278	112	
			0.5	101.55	474	136	

Temp	k	b		calc α	exp α	% deviation
65°C	1.23	1.297	12	6.91	6.82	+ 1.32
			7.5	10.95	10.83	+ 1.10
			5	14.37	14.37	0.00
			3	21.02	21.60	- 2.80
			2	32.68	33.50	- 2.45
			1	70.50	70.00	+ 0.71
			0.5	116.65	110.00	+ 6.04

Despite the higher activity of the 45°C run, so evident on the graphs, it is notable that the initial slope of the growth curve is still the same as for the others. Evidently some surface effect must be held accountable, but there is considerable latitude for conjecture as to its exact nature. The effect becomes further compounded with the passage of time so that the later portion of the curve does not follow the general pattern of the others.

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For purposes of calculation, however, an extrapolated value of "k" was derived and this then arbitrarily broken down into two factors; "k_1"—the expected value of "k" by extrapolation of the other temperature run "k" values, and "k_2"—a theoretical surface effect factor which when incorporated would at least give fair agreement over the early straight line portion of the curve.

It is interesting to note that the calculated results for the $45°$ "α"'s (if no unusual surface effect were present) would give a properly aligned curve located between those of $35°C$ and $65°C$.

In order to show more vividly the problem of surface effects met in this work, sample radio-autographs are attached as Part 1 of the Appendix. The evident contrast is an indication of the surface roughness, cracks, or fissures which play an important role in producing the variation between individual samples of the same temperature run, to say nothing of other complex phenomena which might arise and cause a wide deviation from a general pattern such as happened in the $45°C$ run.
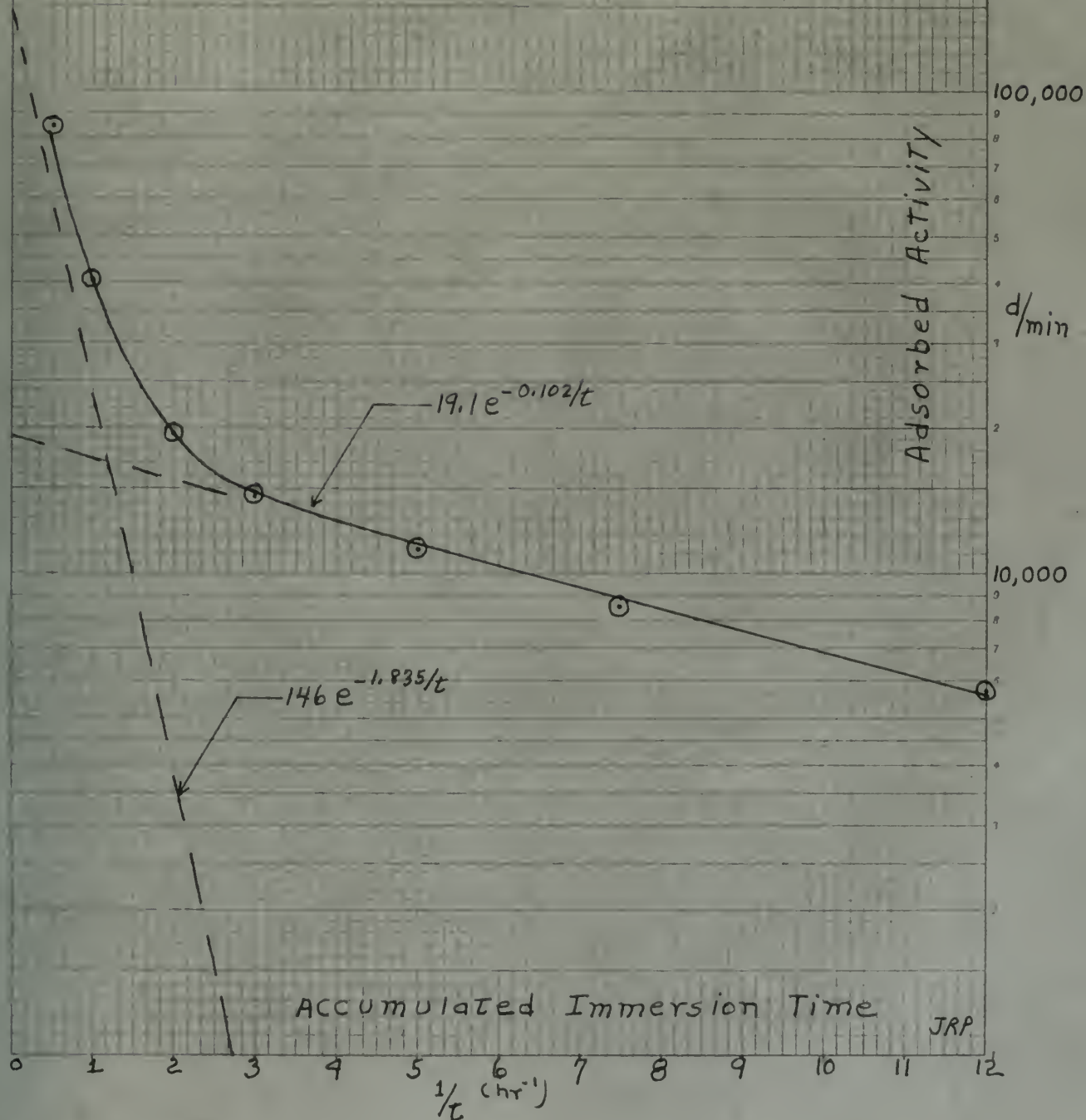
Composite Graph of Experimental Data

100,000

Adsorbed Activity

d/min

10,000

-43°C

-65°C

-35°C

23°C

Accumulated Immersion Time

JRP

1000

0   1   2   3   4   5   6   7   8   9   10   11   12

1/t (hr⁻¹)

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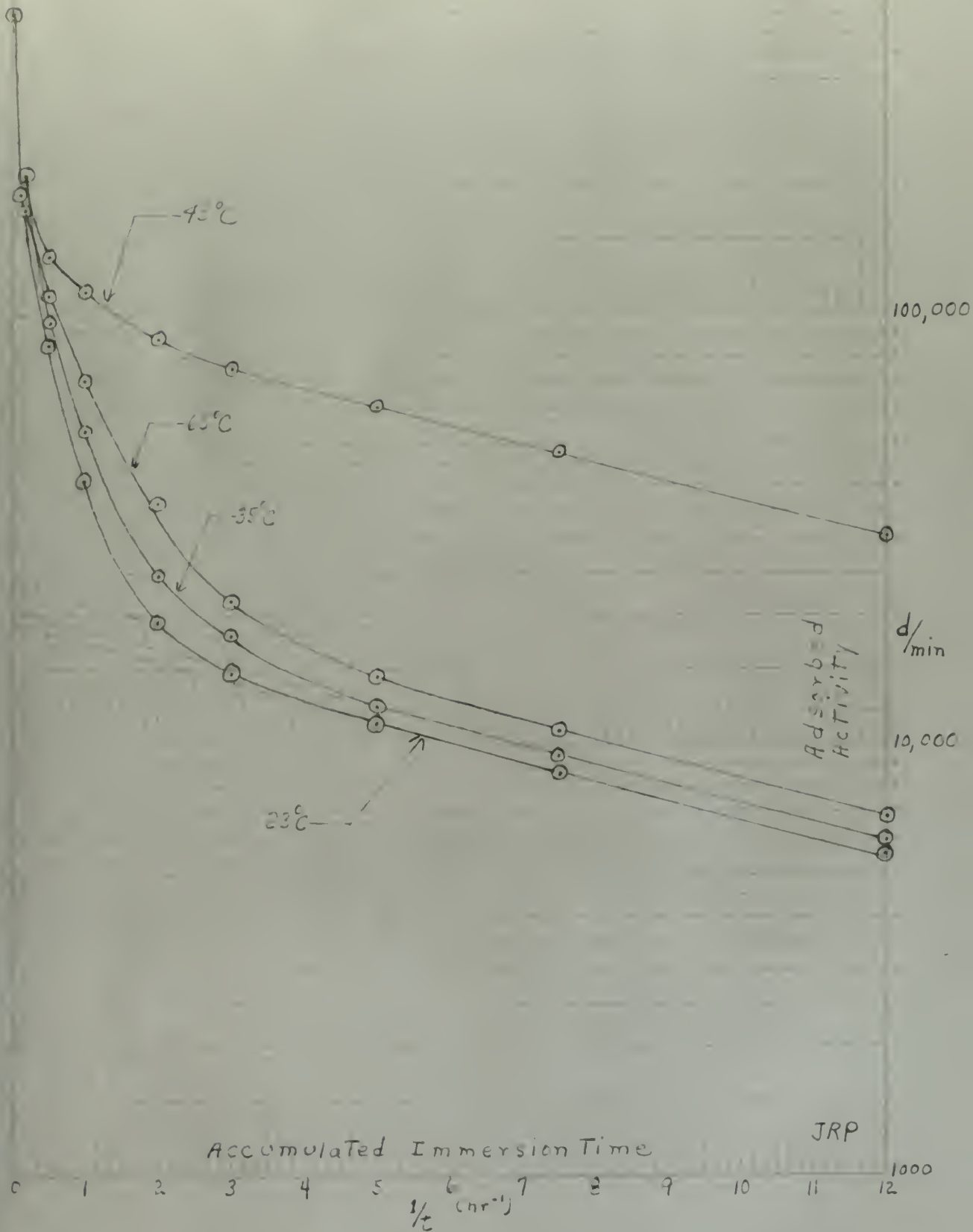
Adsorption of Iodide on Copper

23°C   Initial I^{131} conc. 0.284 $\frac{uc}{ml}$
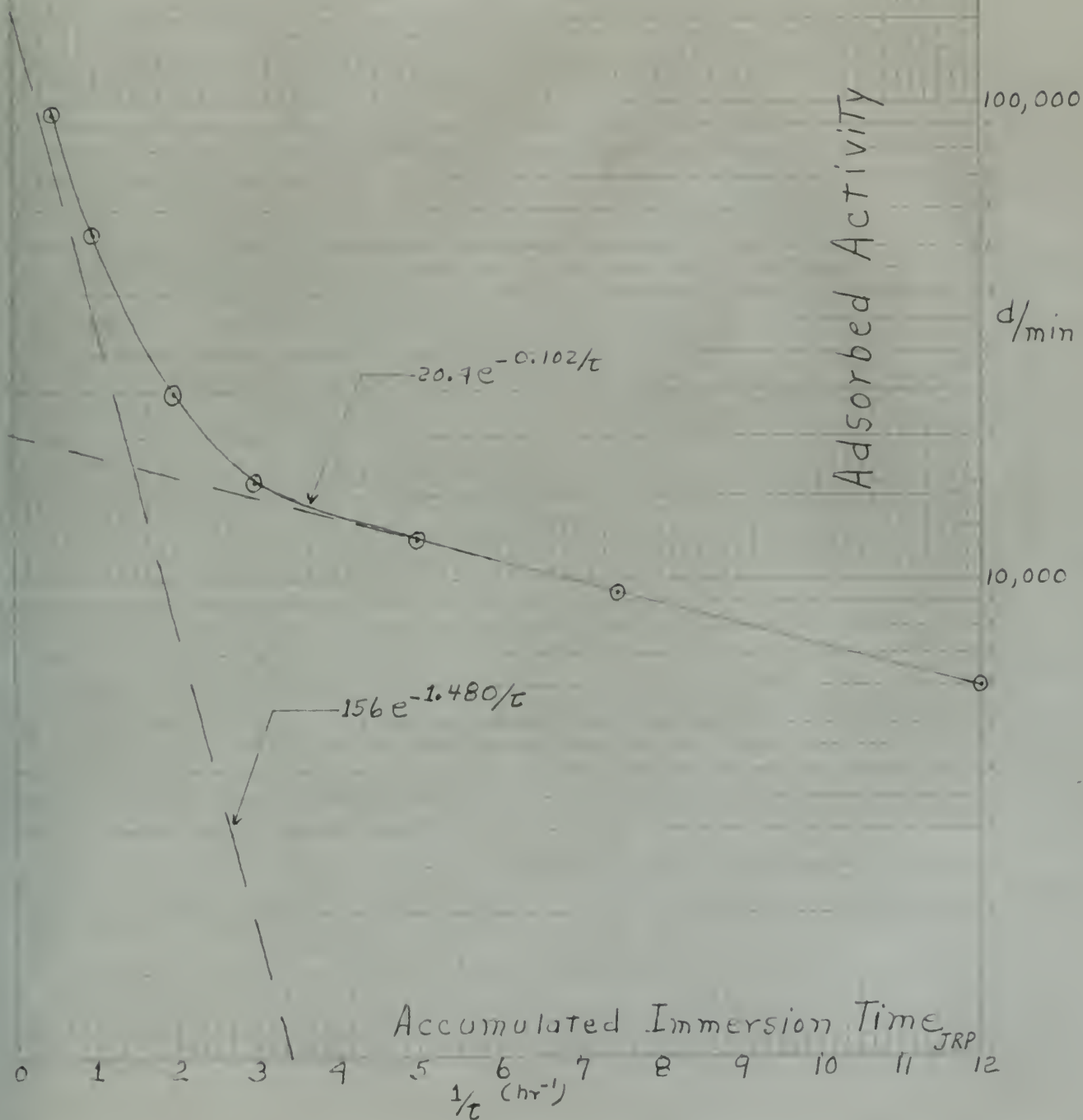
⊙ = Experimental Points

— = Theoretical Curve

$19.1 e^{-0.102/t}$

$146 e^{-1.835/t}$

Adsorbed Activity

d/min

100,000

10,000

Accumulated Immersion Time   JRP.

$\frac{1}{t}$ (hr⁻¹)

0   1   2   3   4   5   6   7   8   9   10   11   12

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Adsorption of Iodide on Copper

35°C   Initial I^{131} conc. 0.269 $\mu c/ml$

⊙ = Experimental Points

— = Theoretical Curve

$20.7 e^{-0.102/t}$

$156 e^{-1.480/t}$

Adsorbed Activity

d/min

100,000

10,000

Accumulated Immersion Time

$1/t$ (hr^{-1})

JRP

0 1 2 3 4 5 6 7 8 9 10 11 12

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Adsorption of Iodide on Copper
45°C   Initial I^{131} conc. 0.275 $\mu c/ml$

⊙ = Experimental Points
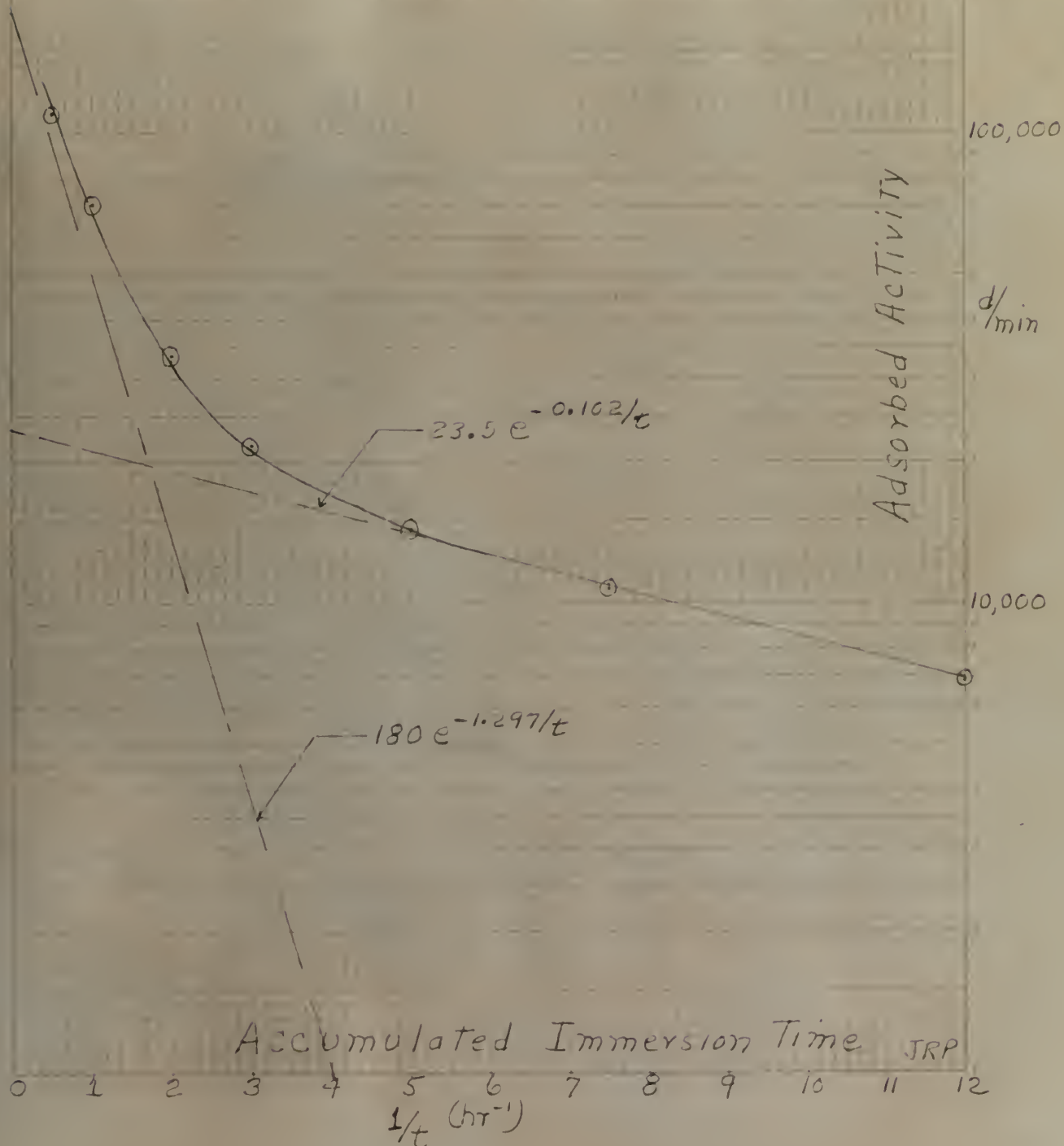
☐ = Experimental Points after correction for postulated surface factor

$-21.4\,e^{-0.102/t}$

$-164\,e^{-1.410/t}$

Accumulated Immersion Time   JRP

Adsorbed Activity

$^d/_{min}$

100,000

10,000

0 1 2 3 4 5 6 7 8 9 10 11 12

$^1/t$ (hr^{-1})

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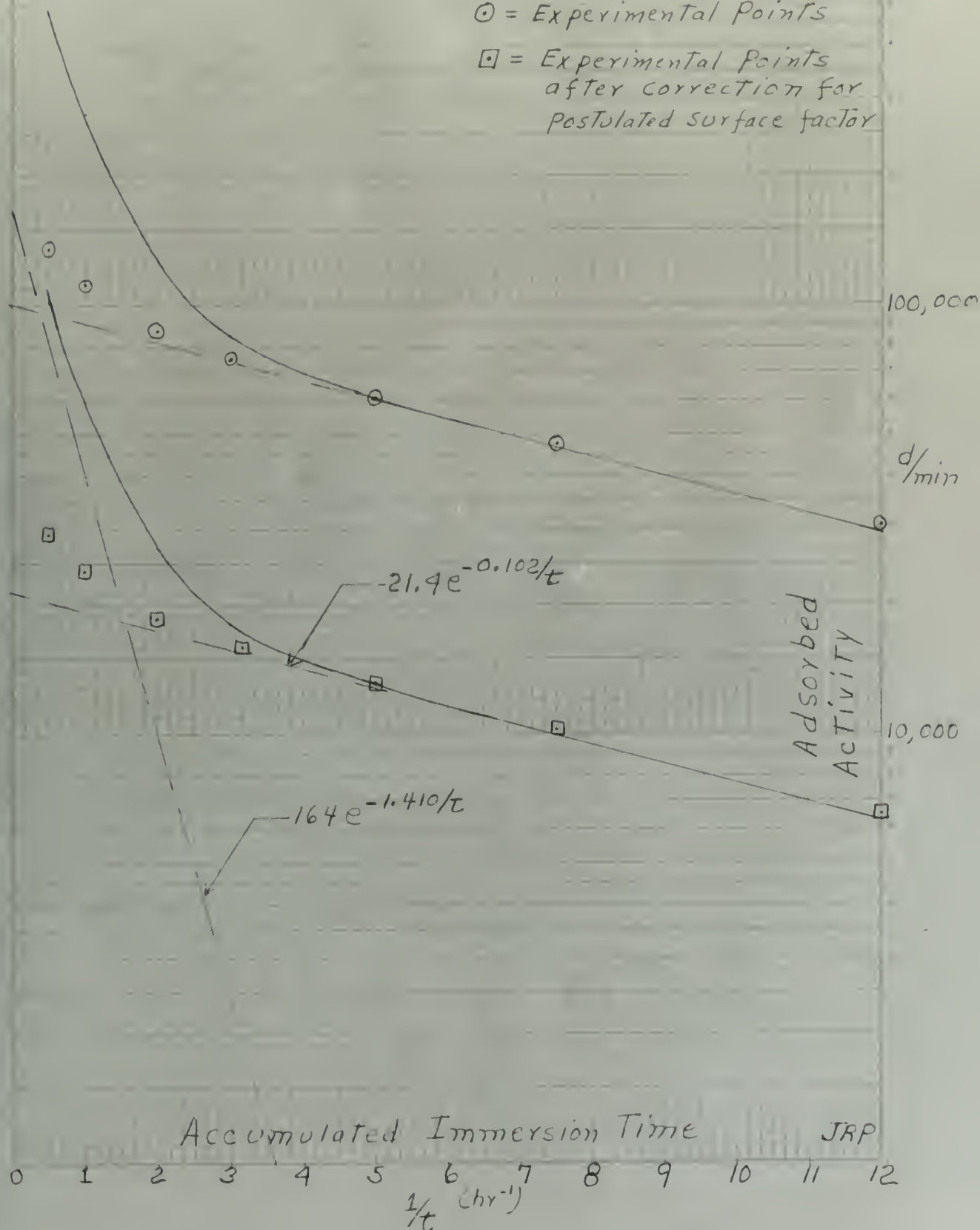
Adsorption of Iodide on Copper

65°C Initial I^{131} conc. 0.260 uc/ml

⊙ = Experimental Points .
— = Theoretical Curve

$23.5 e^{-0.102/t}$

$180 e^{-1.297/t}$

Adsorbed Activity d/min

Accumulated Immersion Time JRP

$1/t$ (hr⁻¹)

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APPENDIX

1. Radio-autographs

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APPENDIX

2. Equipment Calibration Data:

G-M tube was a Tracerlab TGC-1 with 2.3 mg/cm^2 mica end window; serial 2-BV72, and operating voltage 1400 volts.

Standard calibration procedures were followed throughout. In this connection, Bleuler and Goldschmidt's text on "Experimental Nucleonics" (ref. bibliography) proved to be of considerable aid.

Dead time: Dead time was determined by the two source method, and found to be 220.8 micro-seconds.

Counter Efficiency: Co^{60} (0.31 mev β) and UX_2^{234} (2.32 mev β) sources were used to provide the data from which the counter efficiency for I^{131} (0.6 mev β) could be obtained by linear extrapolation.

Shelf Position	Efficiency (for I^{131})
1	0.114
2	0.080
3	0.034
4	0.018

Using the equation, $\mu/\rho = \dfrac{0.02}{E_{max}^{1.33}}$, μ/ρ for I^{131} = 0.0394 cm^2/mg

and computing the f_w factor for the various shelf positions, knowing the density of air and the linear distance from the window of the G-M tube

gave:

Shelf Position	f_w
1	0.871
2	0.852
3	0.790
4	0.733

The above were combined in the equation for counting rate:

$$d/min = \frac{obs.\ cpm}{f_t\ f_w\ f_b\ E}$$

to give: $d/min = \dfrac{obs.\ cpm}{f_t\ F}$ where $F = f_w\ f_b\ E$

and f_b = back scattering factor.

To sum up then, the observed sample counts are first corrected for background and dead time, averaged, and the result divided by the proper value of "F", depending on the shelf used. Values of "F" for the first four shelves are listed below:

Shelf	F
1	0.132
2	0.0905
3	0.0358
4	0.0175

The value of d/min which results from the computation is then further corrected by the proper decay factor back to the chosen "zero time".

All experimental counting rates listed in the data sheets were measured from the # 2 shelf position; except for the initial and final solution concentrations of the 23°C run where # 1 shelf was used.

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